



Formation of epitaxial and polycrystalline films of the electron doped system $\text{La}_{1-x}\text{Ce}_x\text{MnO}_3$ through pulsed laser deposition

C. Mitra, P. Raychaudhuri, S.K. Dhar, A.K. Nigam*, R. Pinto

Department of Condensed Matter Physics & Material Science, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India

Abstract

The polycrystalline $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ manganites do not exist in a single phase in bulk, when prepared through the solid state reaction route as cerium oxide (CeO_2) remains partially unreacted. The resistivity of the bulk $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample shows two metal insulator transition peaks, suggesting the presence of a second (impurity) phase. However, when prepared as thin films by pulsed laser deposition technique, $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ forms in single phase. © 2001 Elsevier Science B.V. All rights reserved.

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In some perovskite-type hole doped manganese oxides $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (where R is a rare earth ion and A is a divalent alkaline earth metal), the colossal magnetoresistance has been the subject of intense studies [1–5]. For a broad range of doping ($0.2 \leq x < 5$), these materials have a paramagnetic to ferromagnetic (FM) transition upon cooling, accompanied by a sharp drop in the resistivity. In the doped materials this behaviour is usually explained by the Zener double exchange (DE) interaction [1,2], where the hopping of electrons between spin aligned Mn^{3+} and Mn^{4+} ions gives rise to an effective ferromagnetic interaction between the Mn^{3+} and Mn^{4+} ions due to strong on-site Hund's coupling.

Since Mn also exists in Mn^{2+} valence state, and hence due to the inherent symmetry, one could also have double exchange between Mn^{3+} and Mn^{2+} giving rise to ferromagnetism and metal insulator transition (MIT) in the case of electron doped samples, where we partially replace Mn^{3+} by Mn^{2+} ions. In an earlier work we have shown that in the layered perovskite manganites of the type $\text{La}_{1.8}\text{Ca}_{1.2}\text{Mn}_2\text{O}_7$, one can indeed obtain an electron doped system by forming the compounds $\text{La}_{1.8}\text{Y}_{0.5}\text{Ca}_{0.7}\text{Mn}_2\text{O}_7$ [6], and that the observed

ferromagnetism and MIT are due to the double exchange between Mn^{3+} and Mn^{2+} . Around the same time, Mandal and Das [7] have shown that partial substitution of the trivalent ion La^{3+} in LaMnO_3 by the tetravalent (Ce^{4+}) state, drives some of the Mn^{3+} ions to a Mn^{2+} state. It has been shown that the system $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$, undergoes an MIT and FM ordering at around 250 K, though they also observed another peak in the resistivity around 225 K, which they could not explain [7].

We have also prepared the polycrystalline bulk $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample following the solid state reaction route prescribed by Mandal and Das [7], and characterized them by powder X-ray diffraction (XRD) method. Our XRD pattern exactly matches the one reported by them. The Rietveld analysis [8] of the XRD pattern (Fig. 1) shows that the sample $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ forms in the Pnma orthorhombic structure similar to that of the hole-doped $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Here we have fitted the data to two different phases, first corresponding to $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$, space group Pnma, and the second phase to unreacted CeO_2 , space group Fm3m. We conclude from our fitting, the presence of at least 20% unreacted CeO_2 . These impurity peaks were mistakenly indexed by Mandal and Das [7] as $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ peaks.

Using these thoroughly ground and mixed polycrystalline specimens as targets, we deposited the films by

* Corresponding author. Fax: +91-22-215-2110.

E-mail address: akn@tifr.res.in (A.K. Nigam).

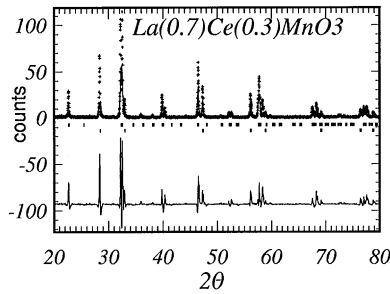


Fig. 1. The X-ray diffraction pattern of $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$, with Rietveld fitting using FULLPROF. ‘+’ indicates the observed pattern, and the straight line indicates the calculated curve. The bottom line shows the difference between the two. The vertical bars below the fitted curve indicate the reflections. The vertical bars in the first line corresponds to the reflections of $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ phase and those in the second line represent the reflections belonging to the second phase (CeO_2).

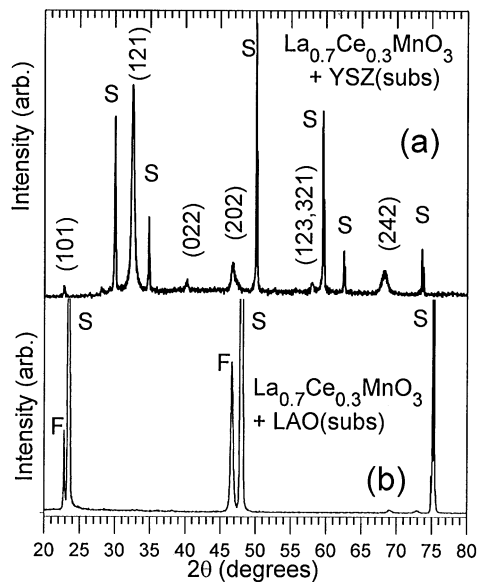


Fig. 2. (a) The XRD pattern of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ polycrystalline film along with the substrate. The substrate peaks are denoted by “S” and the sample (film) peaks are properly indexed. (b) X-ray θ - 2θ scan of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ film grown at 400 mTorr oxygen pressure, with the substrate peaks labelled as “S”, and the film peaks labelled as “F”.

pulsed laser deposition (PLD). The epitaxial films were deposited on a LaAlO_3 (LAO) substrate and the polycrystalline films were deposited on a polycrystalline Yttrium stabilized Zirconia (YSZ) substrate. The films were deposited using a KrF excimer laser in an oxygen atmosphere. The substrates (LaAlO_3 and YSZ) were kept between 750°C and 760°C at all times. The laser energy density was approximately 3 J/cm^2 with a repetition rate of 10 Hz and the laser wavelength was 248 nm. Films

were grown at an oxygen pressure of 400 mTorr. The films were characterized using a Siemens X-ray diffractometer. Fig. 2(a) shows the XRD pattern of the polycrystalline film of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ with the sample peaks identified and labelled distinctly from the substrate (YSZ) peaks. The substrate peaks have been labelled as “S”. Apparently, we do not see any impurity peak in this XRD pattern. Using the space group Pnma, we have indexed the peaks of the XRD pattern shown in Fig. 2(a) and have calculated the lattice parameters of this sample. They are $a = 5.5263\text{ \AA}$, $b = 5.5025\text{ \AA}$, $c = 7.8643\text{ \AA}$.

Coming to the epitaxial film, we have investigated its properties and compared it with the polycrystalline $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample. The XRD θ - 2θ scans showed that the epitaxial film has an orientation $c \perp$ to the film-plane. Fig. 2(b) shows the representative θ - 2θ scan for the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ epitaxial film grown at 400 mTorr. No impurity phase could be detected from the XRD scans in any of the films. The sample peaks (F) are identified and labelled distinctly from the substrate (LAO) peaks (S).

The resistance vs. temperature curve of the bulk polycrystalline $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample, shown in Fig. 3 (inset), has two peaks, one around 250 K and another around 225 K. The peak appearing at 250 K may correspond to the MIT of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ phase and the other peak is presumably due to some impurity phase. However, the resistance of laser ablated $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ epitaxial film shows a single clean MIT peak, as shown in Fig. 3. This suggests that the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ does not exist in single phase when prepared through the solid state reaction route, but it forms in single phase when

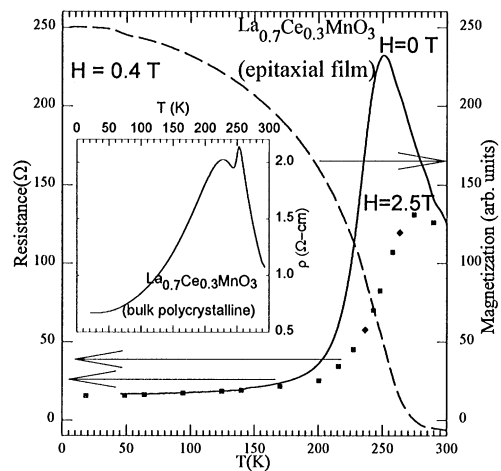


Fig. 3. The resistance vs. temperature plot of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ epitaxial thin film taken at zero field and at a magnetic field (H) of 2.5 T and the magnetization (M) vs. temperature (T) data of the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ epitaxial thin film taken at $H = 0.4\text{ T}$. Inset shows resistivity vs. temperature plot of the bulk polycrystalline $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample.

deposited by pulsed laser ablation. Fig. 3 also shows the resistance vs. temperature data taken in a field of 2.5 T. The MIT temperature is elevated by the application of field and the resistance decreases, thus exhibiting a large magnetoresistance. The magnetization (M) vs. temperature (T) data (taken at 4 kOe) of the epitaxial thin film $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ sample is also shown in Fig. 3. It is clear from Fig. 3 that the MIT temperature (in zero field) coincides with the ferromagnetic ordering temperature (T_c).

In conclusion, we have found that polycrystalline bulk samples of $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ do not form in single phase, when synthesized by solid state reaction route as some amount of CeO_2 remains unreacted. We have also been able to form the $\text{La}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ samples as both polycrystalline and epitaxial films in single phase by PLD, suggesting that it is the energetic laser ablation process which is responsible for the formation of these compounds. The laser ablated thin films not only show single

phase nature when characterized by XRD, but also the unique and clean MIT peak accompanied by a sharp FM transition corroborates the single-phase nature of these films.

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